

# Summary of Recent Chemical Effects Testing

Bruce Letellier
Los Alamos National Laboratory

Kerry Howe and Ashok Gosh University of New Mexico







#### Test Objectives

- Scope chem/temp induced degradation mechanisms contributing to debris generation and head loss
- Motivated by ACRS concern regarding "gelatinous" material reported in TMI at the time of reentry
  - Review existing literature and establish chemical test conditions
  - Corrosion of metals with precipitation of flocculant
    - Rate of corrosion for iron, zinc, aluminum
    - Head-loss effects of chemical precipitation
  - Chemical degradation of fibrous debris beds leading to slow compaction and increasing head loss
  - Degradation/dissolution of nonqualified coatings present in containment







#### **Summary of Results**

- Metal corrosion credible for exposure to borated cooling water
  - UNM tests confirm literature reports at low temp
  - Follow on studies in progress for high temp
- Low solubility leads to precipitation at low concentrations
- Significant head-loss observed in combination with fiber debris beds
- Plant vulnerability depends on surface area of exposed metal and exposure time







# **LOCA Chemical Conditions**

Parameters	T = 0	T = 10	T = 23	T = 15	T = 24	T = 48
	sec	sec	sec	min	hr	hr
Lithium (ppb)	1400	1400	1400	630	115	115
Borate (ppm)	800	800	800	1400	2070	2070
Temperature	40	124	128	118	63	63
°C (°F)	(104)	(255)	(262)	(244)	(145)	(145)
рН	7.7	7.0	7.2	8.4	7.9	7.8
Pressure	0.1	0.38	0.47	0.36	0.14	0.13
Mpa (bar)	(1)	(3.8)	(4.7)	(3.6)	(1.4)	(1.3)

Radiolytic decomposition products not considered as precursor to sump failure







## **Head-loss Test Apparatus**



- Diameter 1/3 of large setup
- Flow meter has 20gpm max
- 10 liter total volume
- Online temperature probe
- Flow valve in the pump outlet
- Continuous pH control
- Pump heats water to ~47 °C
- Replicate measurements with tap water and fiber confirm same response between large and small loops







# Head Loss in Different Chemical Environments

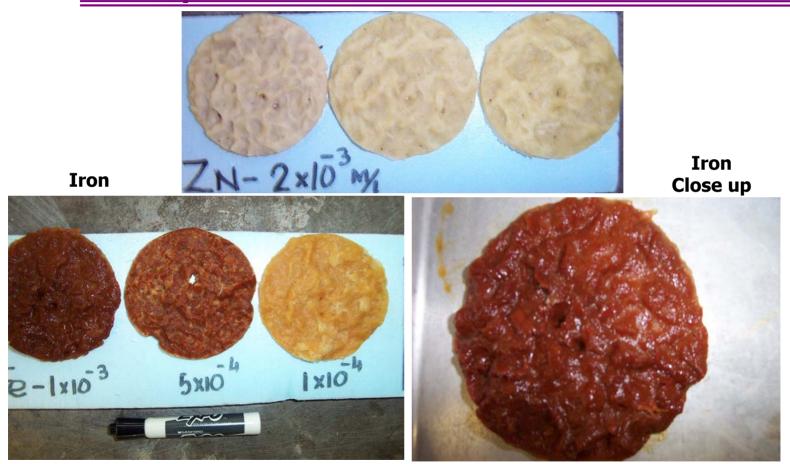
- Tests done in deionized water supplemented by strong buffer solution of boric acid and lithium hydroxide (Calcium hydroxide [ Ca(OH)<sub>2</sub>] added to simulate concrete ablation)
- Fiber bed established
- Metallic salts (representative concentrations) used to induce precipitation
  - Iron nitrate nanohydrate [ Fe(NO<sub>3</sub>)<sub>3</sub> ⋅ 9 H<sub>2</sub>O]
  - Aluminum nitrate nanohydrate [ Al(NO<sub>3</sub>)<sub>3</sub> ⋅ 9 H<sub>2</sub>O]
  - Zinc nitrate hexahydrate [ Zn(NO<sub>3</sub>)<sub>3</sub> · 6 H<sub>2</sub>O]
- Head loss measurement







# Sample Debris Beds



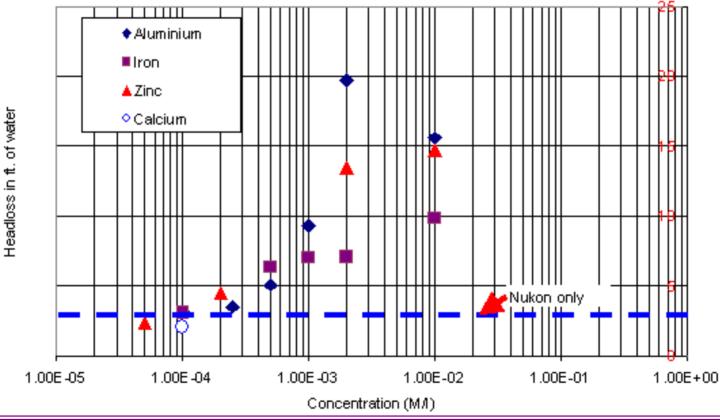






# **Head-Loss Observations**

Headloss with chemical concentration at pH=7









## **Engineering Chemistry Facts**

- Atomic Weights:
  - Al = 27 g/mole
  - Fe = 56 g/mole
  - Zn = 65 g/mole
- 10<sup>-4</sup> M (moles/liter)
  - $Al = 23 lb/10^6 gal$
  - Fe = 47 lb/10<sup>6</sup> gal
  - Zn = 55 lb/10<sup>6</sup> gal

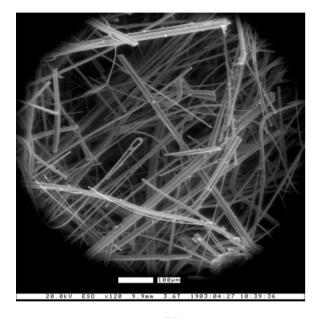
- Threshold of measurable ΔP increase at 10<sup>-4</sup> M
- 7 to 10 ft of additional head loss at 10<sup>-3</sup> M
- 10<sup>-3</sup> M (moles/liter)
  - Al = 0.27 g/10 liter
  - Fe = 0.56 g/10 liter
  - Zn = 0.65 g/10 liter
- Poor solubility of metals reaches saturation at low concentration
- Aluminum nitrate commonly used as water clarity coagulant
- Head-loss *much* more severe than equal mass of particulate

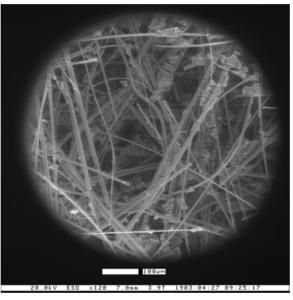


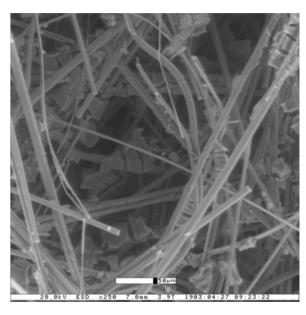




# **ESEM Images of Dry Samples**







**Pure Fiber** 

**Iron Bed** 

**Iron-bed Close Up** 

Apparent adhesion of amorphous material may not permit application of NUREG 6224 head-loss correlation







# Dissolved Metal Source Terms (Leaching Tests)

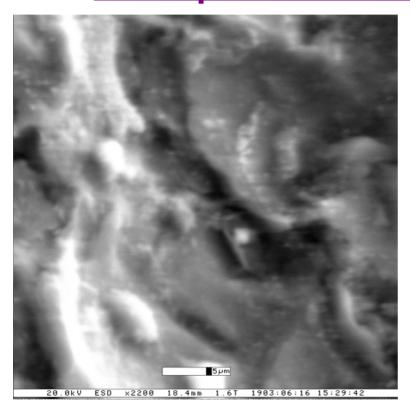
- STUK reports Zn corrosion rates between 0.01 g/m²/hr and 11.3 g/m²/hr under mixed temps and pH
- UNM 11-day immersion tests of zinc granules and bulk coupons confirms lower rate at room temp, pH 7
  - Measured sample mass before and after
  - Analytic concentration measurement of solution
  - Never reached saturation limit
  - Repeating for chips/granules of inorganic zinc primer
- UNM 11-day immersion tests of zinc granules at 80°C, pH 7 presently inconclusive
  - All samples turn black and gain mass
  - Rapid dissolution suspected to reach solubility limit
  - Secondary reaction products different from precipitation?
  - Hard crystalline particulate formed on surfaces
  - Daily test intervals now used to isolate corrosion rate

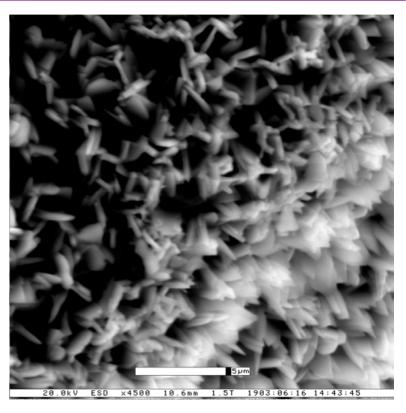






# ESEM of Secondary High Temp Surface Reaction





Clean Zinc Granule

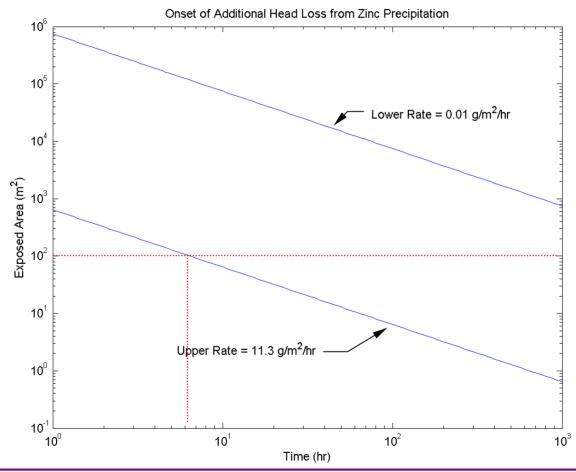
Corroded Zinc Granule







# Preliminary Vulnerability Ranges for Zinc Corrosion









#### Remaining Work

- Incremental leaching cycle to measure high-temp corrosion rate
- Immersion of consumer grade alkyd coating samples to monitor for qualitative degradation mechanisms
- Long-term (24 to 36 hr) small loop head-loss tests to monitor for chemical degradation effects
- Practical correlation of head loss to debris-bed mass
- Documentation of findings in forthcoming NUREG
- Conduct of peer review



